



LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Electronic and Magnetic Properties of $\text{Li}_{1.5}\text{Mn}_{0.5}\text{As}$ Alloys in the Cu_2Sb Structure

C. Y. Fong, L. Damewood, L. H. Yang, C. Felser

December 6, 2012

2013 First International Conference on Solid State and
Materials

Los Angeles, CA, United States

January 30, 2013 through January 31, 2013

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Electronic and magnetic properties of $\text{Li}_{1.5}\text{Mn}_{0.5}\text{As}$ alloys in the Cu_2Sb structure

C. Y. Fong¹, Liam Damewood¹, L. H. Yang², and C. Felser³

¹Department of Physics, University of California, Davis, CA 95616-8677, USA

²H Division, Division, Lawrence Livermore National Laboratory, Livermore, CA 94551, USA

³Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany

Abstract

We investigated two formula-units of $\text{Li}_{1.5}\text{Mn}_{0.5}\text{As}$ alloys, such as Li_3MnAs_2 , in the Cu_2Sb crystal using an *ab-initio* algorithm. By interchanging Mn with each Li located at different positions of Li_4As_2 in the unit cell, four separate alloys are formed. At the optimized lattice constant, two of these alloys are predicted to be ferromagnetic metals and the other two are half metals. The half metallicity of the first two is also explored. Both the modified Slater-Pauling-Kübler rule and the ionic model can characterize the magnetic moments of the half metals.

Key words: ferromagnetic, half metals, bonding properties.

I. Introduction

Compounds formed by group I, group V elements and manganese, Mn, I-Mn-V, such as LiMnAs in cubic structures have recently attracted much interest¹⁻³ for their high antiferromagnetic ordering temperature and large spin-orbit induced anisotropy. They are promising candidates for spintronic materials. There is another class of materials which is a variance of I-Mn-V and is in alloy form, $\text{I}_x\text{Mn}_{1-x}\text{V}$, such as $\text{Li}_{1.5}\text{Mn}_{0.5}\text{As}$. They crystallize in the form of Cu_2Sb , a tetragonal crystal structure, instead of cubic structures. Since it contains Mn and As, one expects that these alloys can be ferromagnetic half metals, such as zinc-blende MnAs ⁴. However, our studies of LiMnAs , in the half Heusler structure⁵ at the optimized lattice constant, shows no half metallicity. This half Heusler compound is not a half metal because Li gives up its electron causing the conduction band edge in the semiconducting channel to be occupied. It will be interesting to ask: since there is more than one Li atom in $\text{Li}_{1.5}\text{Mn}_{0.5}\text{As}$, do the Li atoms give up their electrons and destroy the half metallicity if it exists? To answer these questions, we first consider an alternative structure having an integer number of atoms/formula-unit: Li_3MnAs_2 . In this paper, we restrict ourselves to one Mn in the unit-cell. Thus, the issue of antiferromagnetism is not addressed. We make use of the idea of alloying to decide where to place the Mn in the unit-cell—a Mn atom can substitute any Li atoms in the unit-cell. The following issues are addressed: A. do the properties of these alloys depend on where the Mn is located? If so, more issues are to be addressed: B. can they exhibit ferromagnetic or ferromagnetic half metallic properties? C. if some of them are half metals, what are the values of the lattice constants, total energies, and magnetic moments? Finally, D. for the half metals, can their moments be accounted for by either the modified Slater-Pauling-Kübler rule or the ionic model⁶? The ionic model can suggest whether Li gives up its electron.

In section II, the crystal structure of Cu_2Sb , for an alternate structure of $\text{Li}_{1.5}\text{Mn}_{0.5}\text{As}$ with integer number of atoms/formula-unit, will be discussed. Method of calculations will be presented in section III. Results and discussion will be given in section IV. In section V, we shall give a summary.

II. Crystal structure of Cu_2Sb and the alternative structure of $\text{Li}_{1.5}\text{Mn}_{0.5}\text{As}$

Crystal structure of Cu_2Sb has been analyzed in detail by Pearson⁷. Wyckoff⁸ gives the tetragonal unit-cell having two molecular units. The experimental lattice constants are $a = 3.992 \text{ \AA}$ in the x-y plane and $c = 1.5258 a$ along the z-direction. In the unit-cell, two Cu (1) atoms are at (2a) with coordinates (0, 0, 0) and (0.5, 0.5, 0), two Cu (2), are at (2c) with (0, 0.5, u) and (0.5, 0, -u), where the first two numbers are in fraction of a, while the last number is the fraction of c. Two Sb atoms are at (2c) with coordinates (0, 0.5, u') and (0.5, 0, -u'), where $u' = -0.265$. The unit-cell has the $P4/nmm$ symmetry. Fig. 1 shows the atomic arrangements in the tetragonal cell.

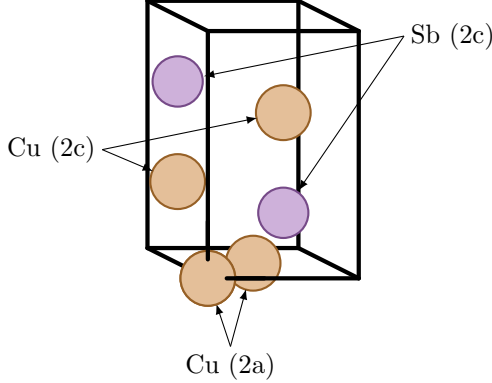


Fig. 1 Two-formula units of Cu_2Sb in the tetragonal unit-cell. Cu atoms are shown in light brown and Sb atoms are shown in purple.

We apply the structure shown in Fig. 1 to Li_3MnAs_2 , not $\text{Li}_{1.5}\text{Mn}_{0.5}\text{As}$. In terms of this alternative structure, Li atoms replace the four Cu atoms and Sb atoms are replaced by the As atoms. For Li_3MnAs_2 , we consider four configurations—Mn replacing each of the four Li atoms, respectively. We label the four cases by Li_j , where $j = 0, 1, 2, 3$. The positions of the Mn at the four sites are summarized in Table I.

Table I. The Position of the Mn atom for each of the four cases. The position is in terms of the fraction of the lattice constants a and c and are indicated by (x, y, z).

j	Mn Position
0 (2a)	(0.00, 0.00, 0.00)
1 (2a)	(0.50, 0.50, 0.00)
2 (2c)	(0.00, 0.50, 0.33)
3 (2c)	(0.50, 0.00, 0.67)

III. Method of calculation

The first-principles code, VASP⁹⁻¹¹, is used for this study. The pseudopotentials of the elements are constructed by the projector augmented wave (PAW) method¹² provided by the code. The Perdew-Burke-Ernzerhof form of the generalized gradient approximation¹³, GGA, is used at this point to avoid any empirical parameters to treat the exchange-correlation between electrons. The spin-orbit interaction is not considered. The basis functions are plane waves with a cutoff energy of 700 eV. The Monkhorst-Pack special \mathbf{k} -point scheme¹⁴, with (15,15,11) specifying the mesh, was used. The total energy and the magnetic moment of each alloy converge better than 1.0 meV and 1.0 μ_B , where μ_B is the Bohr magneton. Due to the alloying, atomic positions in each alloy are relaxed until the components of the forces acting on atoms are less than 0.6 meV/ \AA .

IV. Results and discussion

A. Do the properties of these alloys depend on where the Mn is located?

To address this issue, we determine the optimized lattice constant, a , for the lowest total energy for each alloy. The optimized lattice constant, the associated total energy, the magnetic moment and whether it is a semiconductor, a metal and a half metal are given in Table I. In all cases, the lattice constant in the z -direction, c , is kept the value for Cu_2Sb given in Sec. II.

Among the four cases, Li_0 and Li_1 , the (2a) sites, have a lower energy. But they are not half metals. Li_2 and Li_3 occupying two different (2c) sites have higher total energies. They are, however, half metals. The difference can be attributed to the neighboring configuration of the Mn—in the (2a) cases, Mn is close to only one As, while in cases of (2c) the two As atoms are the neighbors of the Mn atom. Fig. 2 shows Li_1 and Li_2 atomic arrangements after respective relaxations. From the values of the optimized lattice constants and the energetic points of view, the properties of the alloys depend on the location of the Mn atom.

Table II. The optimized lattice constant, total energy, and magnetic moment of the four alloys

Alloy	Lattice constant (Å)	Total energy (eV)	Magnetic moment (μ_B /unit-cell)	Semiconductor, metal, or half-metal?
Li_0 (2a)	4.050	-26.976	3.756	Metal
Li_1 (2a)	4.045	-26.974	3.724	Metal
Li_2 (2c)	3.982	-26.291	4.000	Half-metal
Li_3 (2c)	3.980	-26.291	4.000	Half-metal

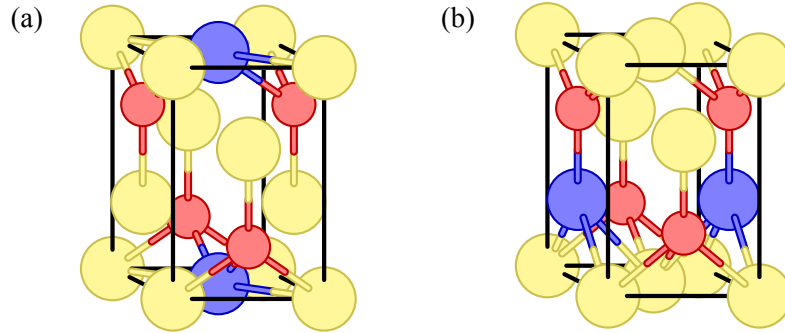


Fig. 2 Atomic arrangements of (a) Li_1 and (b) Li_2 . Li in yellow, Mn in blue and As in red.

B. Can the alloys exhibit ferromagnetic or ferromagnetic half metallic properties?

Even though two of the alloys at their respective optimized lattice constants are not half metals, we can still search the lattice constants for which the alloys show half metallic properties. There is ample evidence that the lattice constant of a half metal needs not to be the same as the optimized lattice constant^{4,15}. In practice, one grows these alloys on substrates, which may not have a perfect match to the optimized lattice constants of the alloys. For each alloy, we found a range of lattice constants at which each alloy exhibits half metallic properties. Since the four alloys can exhibit half metallic properties, we address the issue in the following section.

C. What are the values of the alloys lattice constants and magnetic moments?

In Table III, we list the typical lattice constants, total energies, magnetic moments, and the gaps of the semiconducting channel. The lattice constant $z=c/a$ is kept the same as the experimental value.

The density of states of Li_0 is shown in Fig. 3. In the figure, we identify mainly the states at the top of the valence bands (VB) and the bottom of the conduction bands (CB) in the down spin channel. The top of the VB states originates from the $p_y + p_x$ states of the As with a contribution of 0.257 and Mn $d_{yz} + d_{xz}$ states contributing a fraction of 0.188. The peaks near the bottom of the CB are dominated by Mn d_{xy} and d_{z^2} states with a fraction of 0.851 and 0.716, respectively. With the Fermi energy located in the gap of the semiconducting channel and an integer of magnetic moment, the alloy is a half metal.

Table III. Alloys, lattice constant, magnetic moment, the gap of the semiconducting channel.

Alloy	Lattice constant (Å)	Total energy (eV)	Magnetic moment (μ_B /unit-cell)	Gap (eV)
Li_0 (2a)	4.210	-26.833	4.000	0.915 ↓
Li_1 (2a)	4.215	-26.823	4.000	0.938 ↓
Li_2 (2c)	3.982	-26.291	4.000	0.177 ↓
Li_3 (2c)	3.980	-26.291	4.000	0.161 ↓

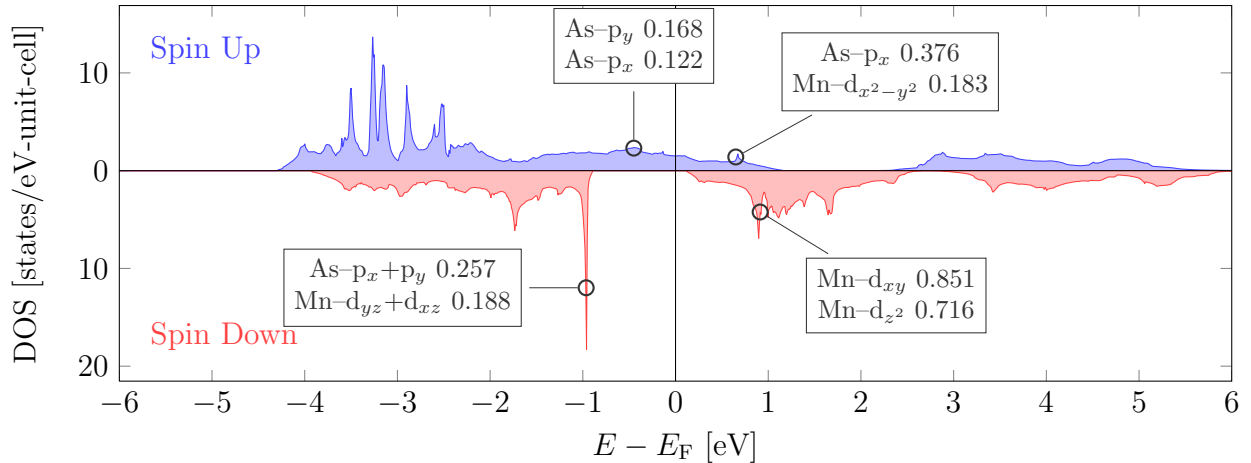


Fig. 3 A representative density of states, DOS, of Li_0 . Peaks near E_F are labeled with the fraction of atomic contributions to those states.

We notice that the lattice constants of Li_0 and Li_1 exhibiting half metallic properties are not far (~ 0.2 Å) from the corresponding optimized values. This is encouraging that the half metallic alloys can be stable. The stability will be reported elsewhere⁵.

D. Can both the modified Slater-Pauling-Kübler rule and the ionic model account for the calculated magnetic moments?

The integer magnetic moments can be accounted for by both the modified Slater-Pauling rule by Kübler¹⁶ or explained by the ionic model^{6,17}. For example, the number of occupied bands in semiconducting channel of alloy Li_0 is 8. The total number electrons/unit-cell is 20. From the rule, its moment should be 4 μ_B /unit-cell. The calculated result is also 4 μ_B /unit-cell. The ionic model works well

for the transition metal under the tetrahedral environment⁶. As seen in Fig. 2, Mn is not under that environment. We propose the following simple picture for ionic model: Each As requires three electrons to fill its $n=4$ shell. All three Li atoms easily give up their electrons; the Mn atom will supply the other three. The remaining four electrons at the Mn contribute to the moment/unit-cell.

V. Summary

In summary, we investigated a new class of ferromagnetic materials, in alloy form, involving group I, group V and the Mn atom, $\text{Li}_{1-x}\text{Mn}_x\text{As}$ but not in a cubic structure. The alloys Li_3MnAs_2 are in the modified Cu_2Sb structure. Two of them are ferromagnetic metals at their respective optimized lattice constants with the Mn occupying the (2a) site having lower energy. They are half metals if the lattice constants differing from the optimized values. The other two with Mn at (2c) site are half metals at their optimized lattice constants and have high total energies with respect to the other two. Both the modified Slater-Pauling-Kübler rule and the ionic model can account for the integer moments.

Acknowledgments

Work at UC Davis was supported in part by the National Science Foundation Grant No. ECCS-1232275. Work at Lawrence Livermore National Laboratory was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

References

- 1 Jungwirth, T., Novák, V., Martí, X., Cukr, M., Máca, F., Shick, A. B., Mašck, J., Horodyská, P., Němec, P., Holý, V., Zemek, J., Kužel, P., Němec, I., Gallagher, B. I., Campion, R. P., Foxon, C. T. & Wunderlich, J. *Phys. Rev. B* **83**, 035321 (2011).
- 2 Novák, V., Cukr, M., Soban, Z., Jungwirth, T., Martí, X., Holý, V., Horodyská, P. & Němec, P. *J. of Cryst. Grow.* **323**, 348 (2011).
- 3 Cava, R., *J. Physics* **4**, 7 (2011).
- 4 Pask, J. E., Yang, L. H., Fong, C. Y., Pickett, W. E. & Dag, S. *Phys. Rev. B* **67**, 224420 (2003).
- 5 Damewood, L. & Fong, C. Y. *Unpublished* (2012).
- 6 Fong, C. Y., Qian, M. C., Liu, K., Yang, L. H. & Pask, J. E. *J. Nanoscience and Nanotechnology* **8**, 3652 (2008).
- 7 Pearson, W. B. *Zeischrift für Kristallographie* **171**, 23 (1985).
- 8 Wyckoff, R. W. G., Vol. 1 (1963).
- 9 VASP, Institut für Theoretische Physik of the Technische Universität, Wien, Austria.
- 10 Kresse, G. & Furthmüller J. *Phys. Rev. B* **54**, 11169 (1996).
- 11 Kresse, G. & Hafner, J. *J. Phys.: Condens. Matter* **6**, 8245 (1994).
- 12 Blochl, P. E. *Phys. Rev. B* **50**, 17953 (1994).
- 13 Perdew, J. P., Burke, K. & Ernzerhof, M. *Phys. Rev. Lett.* **77**, 3865 (1996).
- 14 Monkhorst, H. J. & Pack, J. D. *Phys. Rev. B* **13**, 5188 (1976).
- 15 Akinaga, H., Manago, T. & Shirai, M. *Jpn. J. Appl. Phys. Lett.* **39**, L-1118 (2000).
- 16 Kübler, J. *Physica B+C* **127**, 257 (1984).
- 17 Schwarz, K. J. *Phys. F: Metal Physics* **16**, L211 (1986).